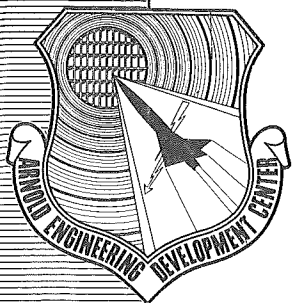


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VACUUM PUMPING BY CRYOSORPTION

By

S. M. Kindall and E. S. J. Wang
Aerospace Environmental Facility
ARO, Inc.

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VACUUM PUMPING BY CRYOSORPTION

By

S. M. Kindall and E. S. J. Wang

Aerospace Environmental Facility

ARO, Inc.

(Paper to be presented at the Ninth National
Vacuum Symposium, October 31 to November 3,
1962, Los Angeles, California.)

October 1962

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ABSTRACT

A method of measuring and analyzing the variation in the rate of adsorption by activated charcoal at 77°K for continuous inflow of nitrogen gas is presented. A set of adsorption parameters is developed for the analysis. Particular attention is given to the meaning of pumping speed for an adsorbent bed of charcoal pellets, and an equation is derived which describes the behavior of pressure in a chamber during continuous adsorption.

PUBLICATION REVIEW

This report has been reviewed and publication is approved.


Donald R. Eastman, Jr.
DCS/Research


Jean A. Jack
Colonel, USAF
DCS/Test

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NOMENCLATURE

| | |
|------------|--|
| A, A_2 | Surface area, ft^2 |
| c | Flow rate dependent constant |
| k | Fundamental adsorption constant |
| M | Molecular weight |
| P | Chamber pressure, torr |
| P_a | Atmospheric pressure, torr |
| P_∞ | Equilibrium pressure, torr |
| P_m | Dynamic pressure, torr |
| P_o | Initial pressure, torr |
| Q | Throughput referenced to chamber temperature |
| R | Gas constant |
| S | Pumping speed, liters/sec |
| T_a | Room temperature |
| T_c | Chamber temperature |
| T_g | Gas temperature |
| V_{ad} | Volume adsorbed, atm cc |
| α | Capture probability |
| γ | Proportionality constant, torr/atm cc |

1.0 INTRODUCTION

Cryosorption is the removal of gases from a vacuum system by means of sorption on an active surface, such as charcoal, at low temperatures. This technique can be traced back to the work of Dewar in 1907 (Ref. 1). He observed a reduction in the pressure of atmospheric gases in a system containing charcoal, when cooled with liquid air. The pressure loss was far greater than could be expected from the cooling alone.

Since that work, extensive studies of adsorption have been carried out. The work of Freundlich (Ref. 2), Langmuir (Ref. 3), Brunauer, Emmett, and Teller (Ref. 4) has led to a fairly complete understanding of the equilibrium between the gas phase and the adsorbed phase. There also has been a lesser amount of work on the rates of sorption. Of particular interest is the work by Bangham and Burt (Ref. 5), McBain (Ref. 6), and by Barrer and Ibbitson (Ref. 7), who studied adsorption from the standpoint of chemical kinetics and postulated a set of sorption mechanisms, including surface migration and diffusion, which lead to equations compatible with the experimental data.

The rate of sorption is very high for clean adsorbents but decreases as the surface approaches saturation. This characteristic makes sorption pumping particularly attractive for applications where continuous pumping is not required (Refs. 8 and 9), but the gas inflow rate may be high.

One such application is in high altitude and space environmental simulation, where there is a test requirement for firing small guidance rockets in a vacuum system. The products of combustion from such a firing present a heavy gas load to the vacuum system, although the firing normally is only a few seconds in duration. For this reason, a study of cryosorption has been undertaken at the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), with the objective of obtaining information for the design of a cryosorption pump.

This report is concerned with the determination of the variation of pumping speed with the amount of gas adsorbed and with the rate of adsorption. In order to efficiently measure these effects, an interrupted

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flow technique has been used which greatly facilitates the interpretation of the results. This technique is similar to the one used in the determination of pumping speed in cryopumping (Ref. 10). The work reported here is concerned with an experimental study of the adsorption of nitrogen on charcoal at 77°K, and deals with the analytical development of the dynamic behavior of cryosorption pumping.

2.0 EXPERIMENTAL

Experimental work was carried out in a stainless steel chamber, 6 inches in diameter and 27 inches long, cooled peripherially with liquid nitrogen. The adsorbent bed consisted of 1/8-inch Columbia activated charcoal pellets packed to 0.5-inch depth in a 5-inch by 10-inch liquid-nitrogen-cooled copper tray. Figure 1 shows the schematic diagram of the vacuum chamber; details of the experimental procedure can be found in Ref. 11.

Two types of measurements were made. One involved monitoring the pressure-time relationship under a continuous inflow condition, and the other used the interrupted flow technique to give an incremental pressure rise curve. In both cases, continuous pressure recordings were made. An example of a continuous run for an inleakage rate of 0.34 atm cc/sec for an adsorbent bed of charcoal pellets is shown in Fig. 2. A discontinuous run for an inflow rate of 0.01 atm cc/sec of nitrogen gas on the same adsorbent bed is shown in Fig. 3.

3.0 ANALYSIS OF DYNAMIC ADSORPTION

Most adsorption parameters are defined for adsorption bed equilibrium conditions where no gas load is introduced simultaneously to the system. Consequently, they are not directly applicable to the analysis of dynamic adsorption, and a new set of adsorption parameters is needed. There is no simple analytical treatment which can explain the dynamic behavior of a cryosorption pump with a constant gas load (Ref. 12). The pressure-time curve of a continuous adsorption run, as represented in Fig. 2, will not by itself give pumping speed and yield data on adsorption parameters useful to predict the performance of a cryosorption pump under different conditions. The necessary requirement for parameters in dynamic adsorption is that they be independent of time, as in the case of equilibrium adsorption. It can be shown that the pumping speed in dynamic adsorption is related to the volume of gas adsorbed and the inflow rate to the system. At a constant

known flow rate, it is possible to relate time and the amount of gas adsorbed with the parameters. The following sections describe the empirical development of parameters for the analysis of dynamic adsorption.

3.1 DYNAMIC PRESSURE VS EQUILIBRIUM PRESSURE

In the interrupted flow technique, as represented in Fig. 3, two pressure terms can be obtained for each flow termination: P_m , the dynamic pressure at the instant of flow termination, and P_∞ , the equilibrium pressure obtained after flow termination. Figure 4 illustrates the definition of P_m , P_∞ , and the initial pressure, P_0 . When $P_m - P_\infty$ is plotted versus P_m for the various flow terminations of Fig. 3, a straight line relationship is obtained as shown in Fig. 5. This relationship can be expressed as:

$$P_m - P_\infty = kP_m + c \quad (1)$$

where k and c are constants. Rearranging Eq. (1) gives

$$(1 - k)P_m = P_\infty + c \quad (2)$$

This linear relationship between P_m and P_∞ is a useful tool in the study of dynamic adsorption. The constant c is related to the nitrogen inflow rate, but k is independent of flow rate, as demonstrated in Fig. 6 where the quantity $(P_m - P_\infty) - c$ is plotted versus P_m for a range of flow rates. The parameter k is a property of the charcoal adsorbent. It can be seen from Fig. 6 that the experimental value for k is 0.625.

By assuming the chamber pressure, P , in the continuous flow runs to be the same as the dynamic pressure, P_m , in the interrupted flow runs, Eq. (1) can be restated as follows:

$$(1 - k)P = P_\infty + c \quad (3)$$

It should be pointed out that Eq. (3) can be valid only after the pattern of steady pressure rise is established in the continuous flow run.

3.2 ADSORPTION ISOTHERM

Knowing the constant flow rate and the time durations of flow, the interrupted flow technique also provides a means of establishing a relationship between P_∞ , the equilibrium pressure, and V_{ad} , the volume adsorbed. The isotherms obtained by this technique are no different from those measured by other equilibrium methods. A typical plot for charcoal adsorption

of nitrogen at 77°K is shown in Fig. 7. A collection of isotherms for several tests of charcoal adsorption of nitrogen gas using different flow rates is shown in Fig. 8. The linear relationship obtained in these two graphs indicates that Henry's law holds for adsorption at low pressures. The adsorption isotherm can be expressed as

$$P_{\infty} = \gamma V_{ad} \quad (4)$$

where γ is a proportionality constant and can be considered as another important parameter in dynamic adsorption. The average γ in Fig. 7 is 3.5×10^{-6} torr/atm cc.

The straight line in Fig. 7 does not actually pass through the origin, because the initial pressure of the chamber, P_0 , is never zero and there exists an initial quantity of gas adsorbed at time zero. For pressures in the 10^{-5} torr region or higher, the initial volume adsorbed can be neglected. If, however, calculations were to be made in the 10^{-7} torr region, this initial volume of gas in the charcoal would be accounted for.

These isotherms are obtained with an adsorbent bed having surface area A . For the adsorbent bed of another surface area, A_2 , the isotherm expression would become

$$P_{\infty} = \frac{\gamma A}{A_2} V_{ad} \quad (5)$$

3.3 DYNAMIC PRESSURE AS A FUNCTION OF TIME

The pressure-time curve, as represented in Fig. 2, for a continuous flow run starts from an equilibrium pressure prior to the initiation of inleakage, passes through a transient region, and continues to a nonequilibrium but steady-state region characterized by a nearly linear rise in pressure with time.

The dynamic pressure can be expressed in terms of V_{ad} by substituting Eq. (4) into Eq. (3):

$$P = \frac{\gamma}{1-k} V_{ad} + \frac{c}{1-k} \quad (6)$$

Equation 6 can be used to describe the nearly linear portion of the pressure-time curve. It is convenient to refer to this portion as the steady-state portion. Equation (3) is not applicable in the transient region. The use of Eq. (3) in constructing Eq. (6) implies that the transition from initial pressure to the steady-state portion in Fig. 2 occurs instantaneously. In the actual case, there is a small transient time involved, as can be seen in

Fig. 2. The magnitude of this initial pressure rise from initial pressure, P_0 , through the transient region, is expressed by $c/(1-k)$ in Eq. (6). Let $c/(1-k)$ be denoted by ΔP and V_{ad} be expressed $(dV/dt)_{atm} t$, where $(dV/dt)_{atm}$ is the rate of inleakage in atm cc/sec and t is the time duration of inleakage. Equation (6) then becomes

$$P = \frac{\gamma}{1-k} \left(\frac{dV}{dt} \right)_{atm} t + \Delta P \quad (7)$$

ΔP can be related to the definition of the conventional pumping speed, S , i. e.,

$$S = Q/\Delta P \quad (8)$$

where Q is the throughput attributable to metered inflow at chamber temperature.

The throughput can be expressed as

$$Q = P_a \left(\frac{dV}{dt} \right)_{atm} \frac{T_c}{T_a} \quad (9)$$

where P_a is the atmospheric pressure, T_c is the chamber temperature, and T_a is the room temperature.

In the free-molecule region, the pumping speed (Ref. 10) can be alternately expressed as

$$S = \alpha A \sqrt{\frac{RT_g}{2\pi M}} = \alpha A \sqrt{\frac{RT_c}{2\pi M}} \quad (10)$$

where R is the gas constant; T_g is the gas temperature, which is equivalent to chamber temperature, T_c in the present case; M is the molecular weight; A is the surface area of the adsorbent; and α is the capture probability.

Substituting Eqs. (8), (9), and (10), Eq. (7) gives the expression for the dynamic pressure:

$$P = \frac{\gamma}{1-k} \left(\frac{dV}{dt} \right)_{atm} t + \frac{P_a \left(\frac{dV}{dt} \right)_{atm} \frac{T_c}{T_a}}{\alpha A \sqrt{\frac{RT_c}{2\pi M}}} \quad (11)$$

In order to express the dynamic pressure for a chamber with the same adsorbent having a different surface area, A_2 , Eq. (11) becomes

$$P = \frac{\gamma}{1-k} \frac{A}{A_2} \left(\frac{dV}{dt} \right)_{atm} t + \frac{P_a \left(\frac{dV}{dt} \right)_{atm} \frac{T_c}{T_a}}{\alpha A_2 \sqrt{\frac{RT_c}{2\pi M}}} \quad (12)$$

3.4 APPLICATION OF ADSORPTION PARAMETERS

As has been previously stated, the adsorption parameters are obtained by the interrupted flow technique. However, their usefulness depends on how well they can be applied to the study of the pressure-time curves for the continuous inleakage runs. The values of γ and k cannot be measured individually from a continuous run, but the term $\gamma/(1 - k)$ can be determined from the slope of the steady-state portion of the pressure-time curve. This was done for four continuous inleakage runs with flow rate varying as shown in Fig. 9. By setting k equal to 0.625, as obtained from the interrupted flow technique (Fig. 6), the γ value for each of the four runs was calculated from $\gamma/(1 - k)$. The average γ for the runs in Fig. 9 is 1.8×10^{-6} torr/atm cc. This agrees well with the average γ value of 3.5×10^{-6} torr/atm cc from the collection of runs shown in Fig. 8.

Thus far, the correspondence of parameters has been shown between interrupted flow runs and continuous flow runs with the same adsorbent surface area in the same small chamber. A large cryosorption pump was also built at AEDC for the study of nozzle flow in an ejector diffuser under vacuum (Ref. 13). It contains a 26.5-ft² surface area of charcoal pellets cooled at liquid-nitrogen temperature inside a chamber that is 11.3 cu ft in volume. The nitrogen flow rate was 1.9 atm cu ft/min. Since all aspects of the cryosorption pump are similar to that described earlier, except for the difference in surface area and volume, the pressure-time curve from a continuous run for this pumping system was evaluated to test the usefulness of the adsorption parameters. Figure 10 presents the pressure-time curve for a nitrogen flow rate of 1.9 standard cu ft/min. The γ of Fig. 10 is found to be 1.85×10^{-6} torr/atm cc, by using the same k value as in the estimation. This is in very good agreement with the γ value from Fig. 9.

3.5 ULTIMATE PRESSURE ATTAINABLE AND PUMPING SPEED

In evaluating a vacuum pumping means, attention will usually focus on two areas: the ultimate vacuum attainable and the pumping speed. The objective of this investigation, however, is to establish an understanding of the dynamic behavior of cryosorption pumping. Therefore, no effort has been expended toward achieving the ultimate vacuum attainable. However, there are many predictions as to the ultimate vacuum attainable by cryosorption, including the interesting dissertation by Hobson (Ref. 14) which predicts a vacuum below 10^{-23} torr by adsorption at 4°K. During the adsorption experiments reported herein, an equilibrium pressure of 10^{-9} torr was initially obtained when the vacuum chamber, 12 liters in volume

and 10^{-4} torr in pressure, was pumped down with a 50-sq-in., charcoal paste, adsorbent surface area at 77°K. This chamber has a leak rate of about 1×10^{-4} atm cc/sec; therefore, it is felt that the ultimate vacuum attainable for N₂ adsorption by charcoal at 77°K will be appreciably below 10^{-9} torr.

The definition of pumping speed for a conventional diffusion pump is not quite applicable to cryosorption pumping. In cryosorption, pumping speed is not constant at any time because the rate of adsorption and the amount of gas adsorbed are continuously changing. In order to illustrate the difference in the pumping characteristics between a cryosorption pump and a conventional diffusion pump, a pressure-time curve for each is presented in Fig. 11.

For a constant inflow rate, the pressure-time curve for a diffusion pump will reach a constant pressure when the rate of inflow is equal to the pumping speed of the pump, whereas the pressure-time curve for an adsorption pump will show a small but continuous pressure rise. This pressure rise in the adsorption pump indicates that its pumping speed decreases with time.

Aside from the continuous pressure rise in the adsorption pump curve, there is a considerable difference in the nature of the transient portion of the two curves. The transient position is the initial pressure rise resulting from the start of inflow of gas to the chamber and before a steady trend of pressure rise is established. The pressure rise in the transient portion was denoted earlier by ΔP . The transient portion of the pressure-time curve for an oil diffusion pump is adequately described by an expression (Ref. 15) involving one exponential term $E(1 - e^{-ft})$ where E and f are constants, whereas the adsorption pump curve is found to require an expression having three such exponential terms, the constants of which are discrete functions of the volume adsorbed (Ref. 11).

The pumping speed of an adsorption pump is at its maximum when the transient pressure rise is equal to ΔP . It can be expressed either by the free-molecule flow equation, as stated in Eq. (10), or by Eq. (8). As the pumping process continues, the difference between dynamic and equilibrium pressures increases. The ΔP in Eq. (8) will become $P - P_{\infty}$.

For the steady-state region,

$$P - P_{\infty} = kP + c \quad (13)$$

The expression for S in Eq. (8) can therefore be extended to include the variable adsorption rate of the steady-state region.

That is,

$$S = \frac{Q}{kP + c} \quad (14)$$

For most pumping speed calculations, c may be safely neglected; therefore

$$S = \frac{Q}{kP} \quad (15)$$

Equation (18) implies that the cryosorption pumping speed is a function of pressure, and therefore it also is a function of volume adsorbed. It should be pointed out that this definition of pumping speed applies only to the steady-state portion of the continuous flow runs.

4.0 CONCLUSIONS

The mechanism of vacuum cryosorption has been studied by a systematic experimental treatment. Through the use of an interrupted flow technique, it is possible to define a set of adsorption parameters which allows the successful prediction of the behavior of dynamic adsorption.

Among the four parameters, the linear relationship between dynamic and equilibrium pressure is the foundation of the entire experimental treatment. For each dynamic adsorption system, a knowledge of the adsorption parameters can be used to describe the pressure-time relationship in any vacuum chamber using activated charcoal at 77°K for various surface areas and nitrogen gas flow rates.

The physical significance of the pumping speed of a cryosorption pump is presented. With the assistance of adsorption parameters, the pumping speed can be defined and measured in a simple manner.

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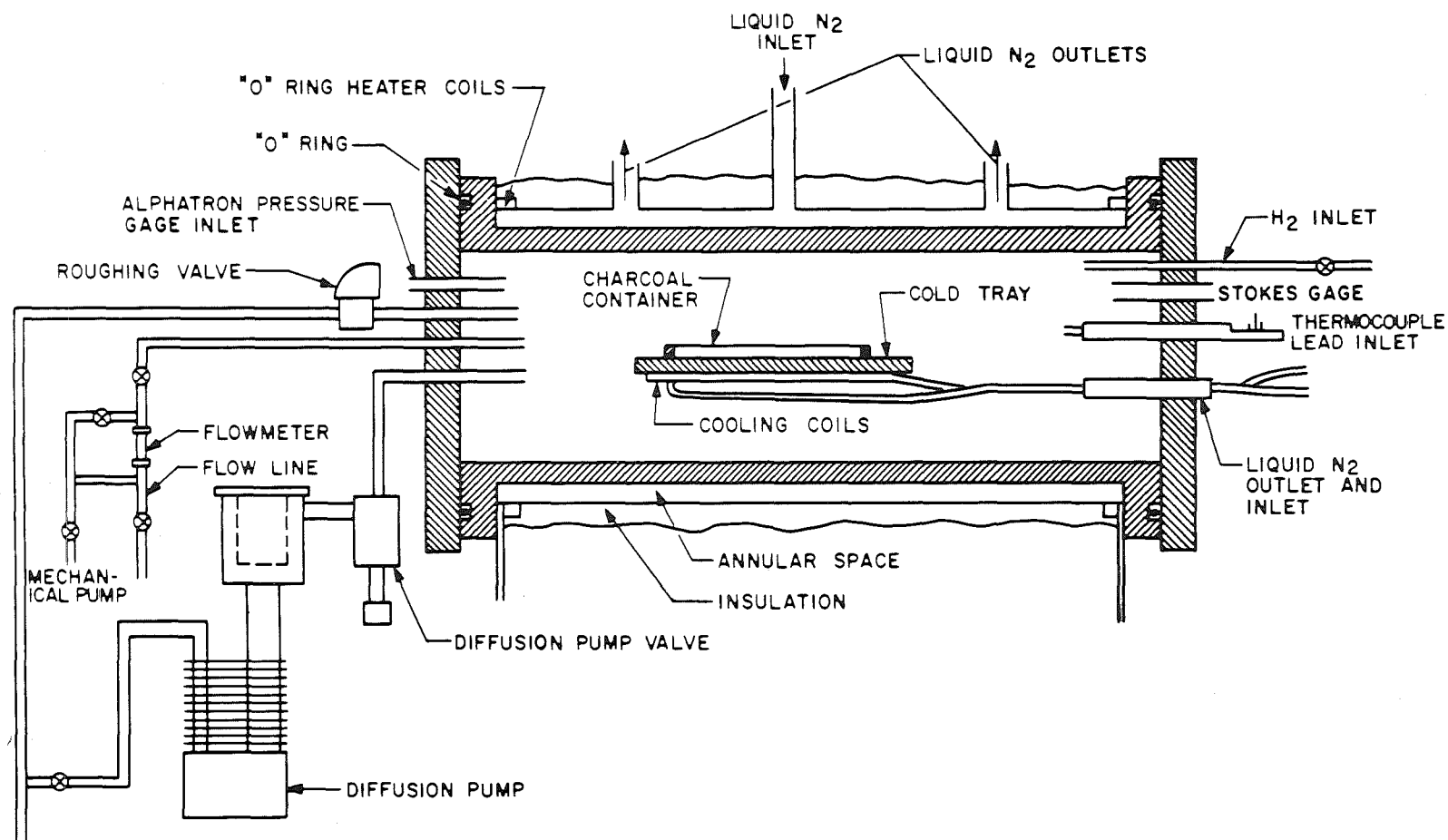


Fig. 1 Adsorption Chamber

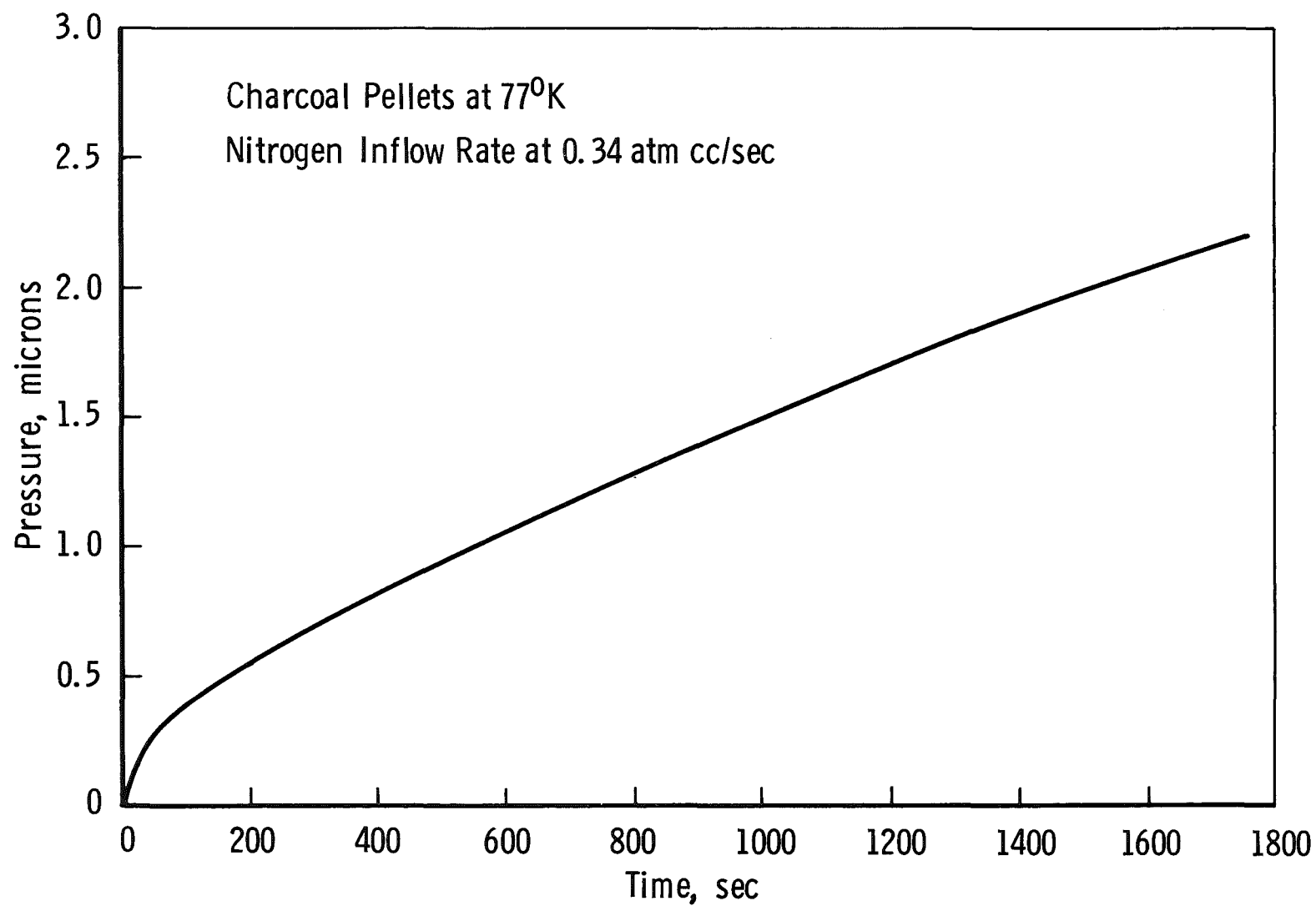


Fig. 2 Charcoal Adsorption of Nitrogen Gas during a Continuous Run

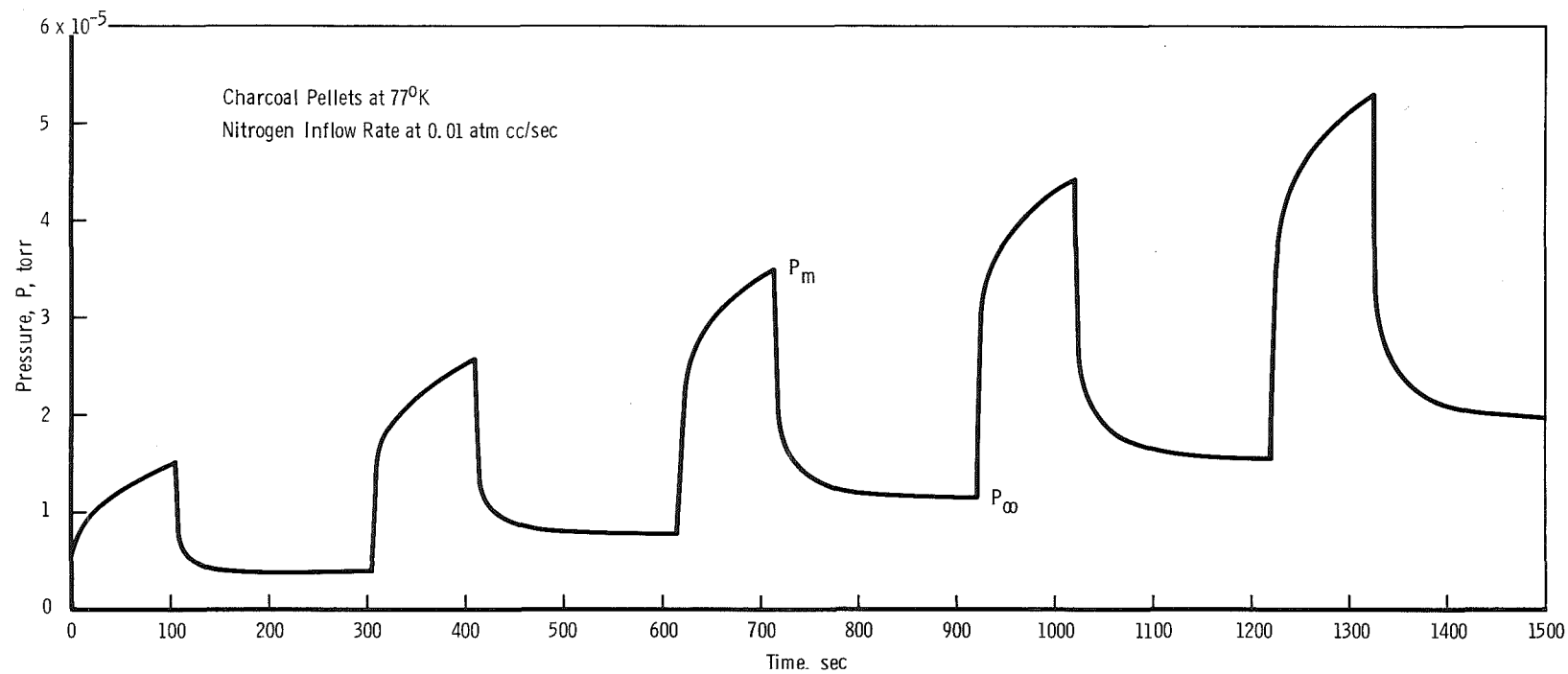


Fig. 3 Charcoal Adsorption of Nitrogen Gas during a Discontinuous Run

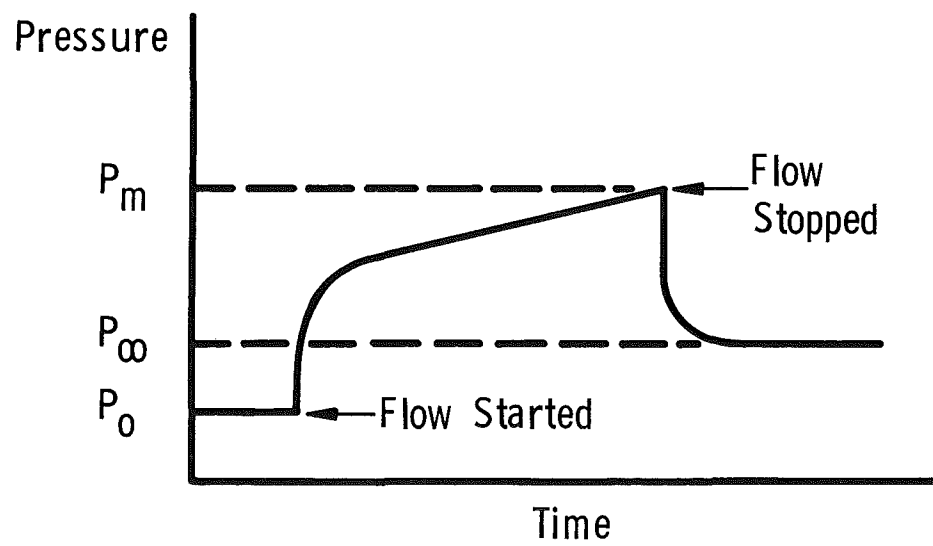


Fig. 4 Relationships between P_m , P_0 , and P_∞

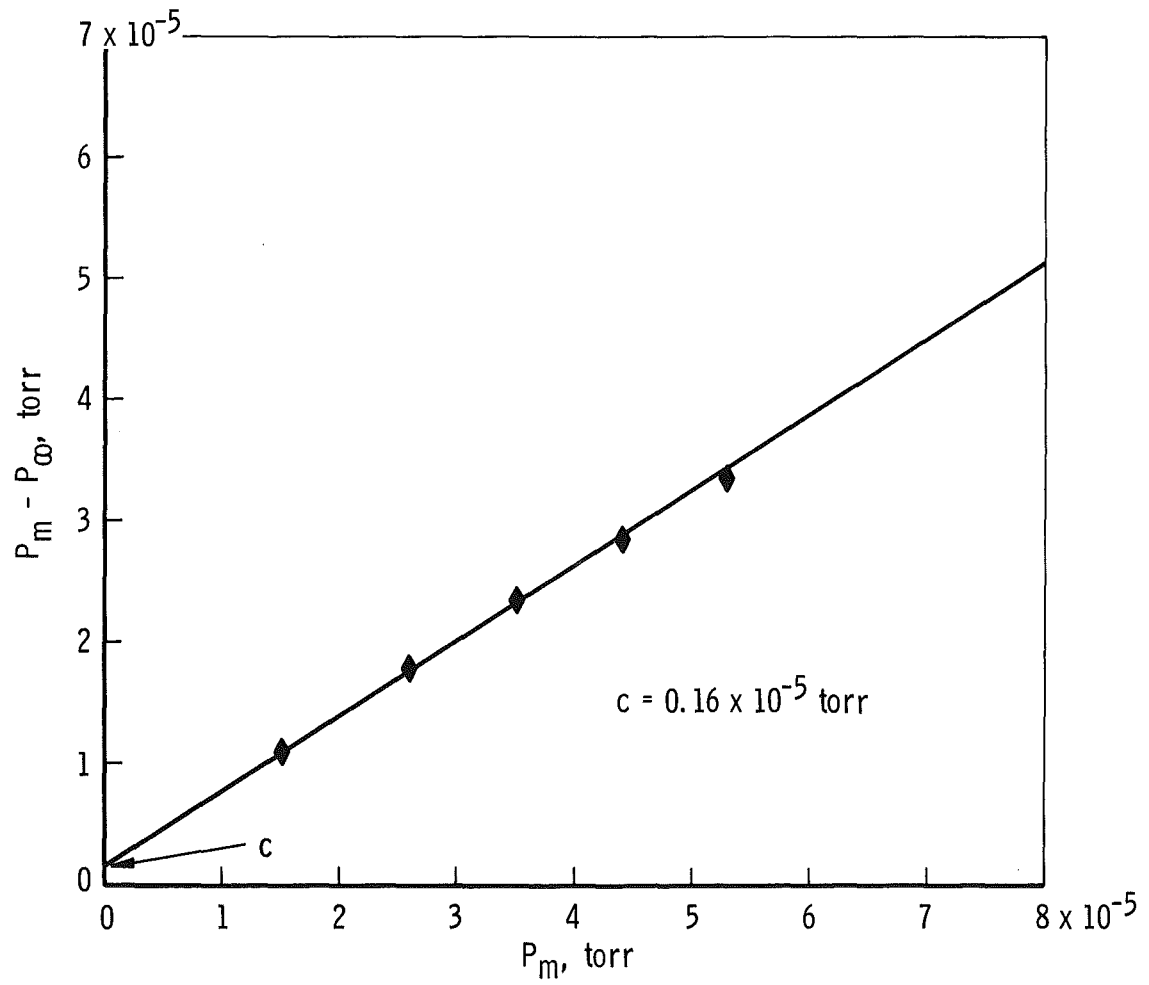


Fig. 5 Variation of $P_m - P_\infty$ with P_m for a Discontinuous Run

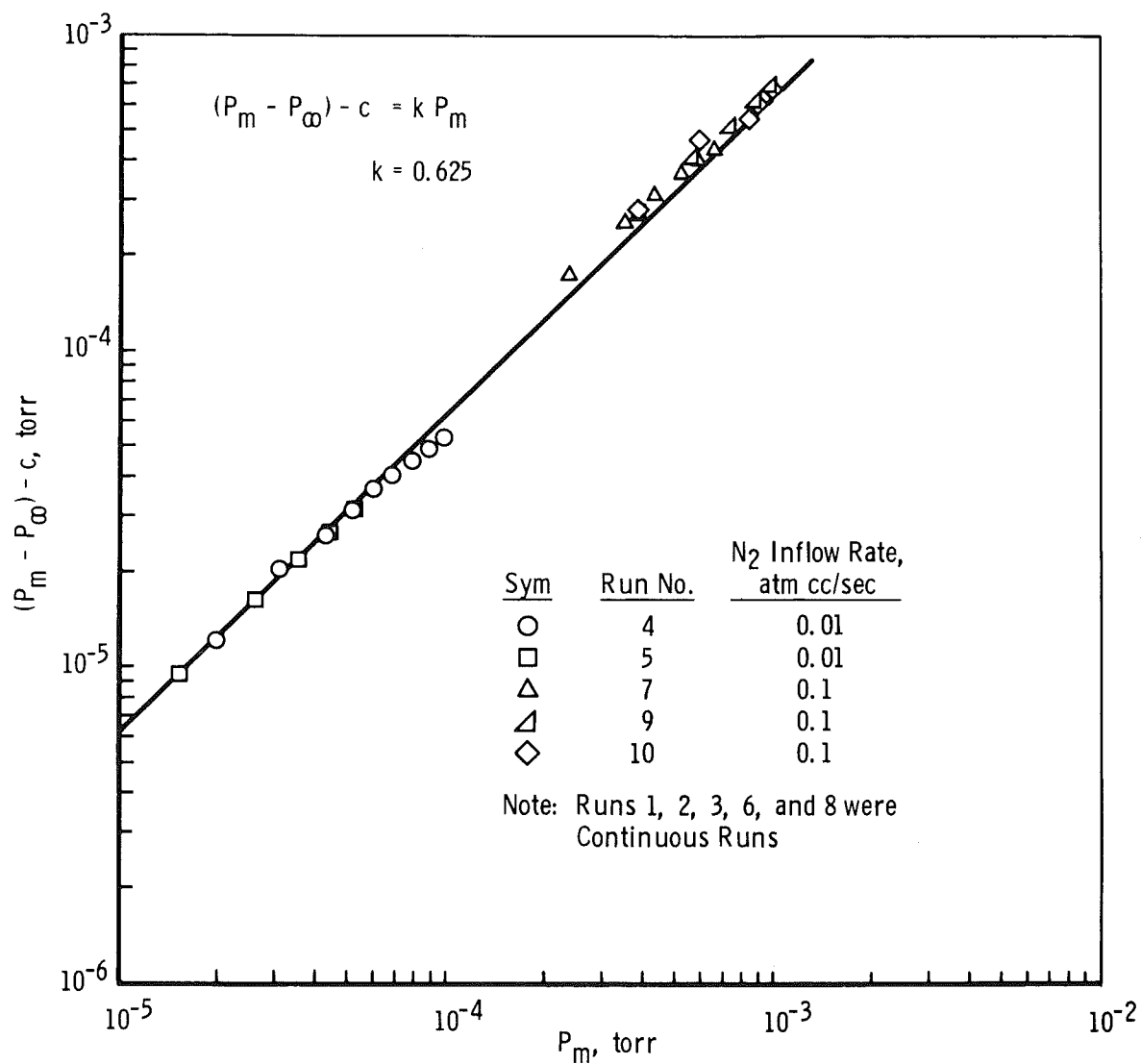


Fig. 6 Variation of $P_m - P_\infty$ with P_m for a Collection of Runs

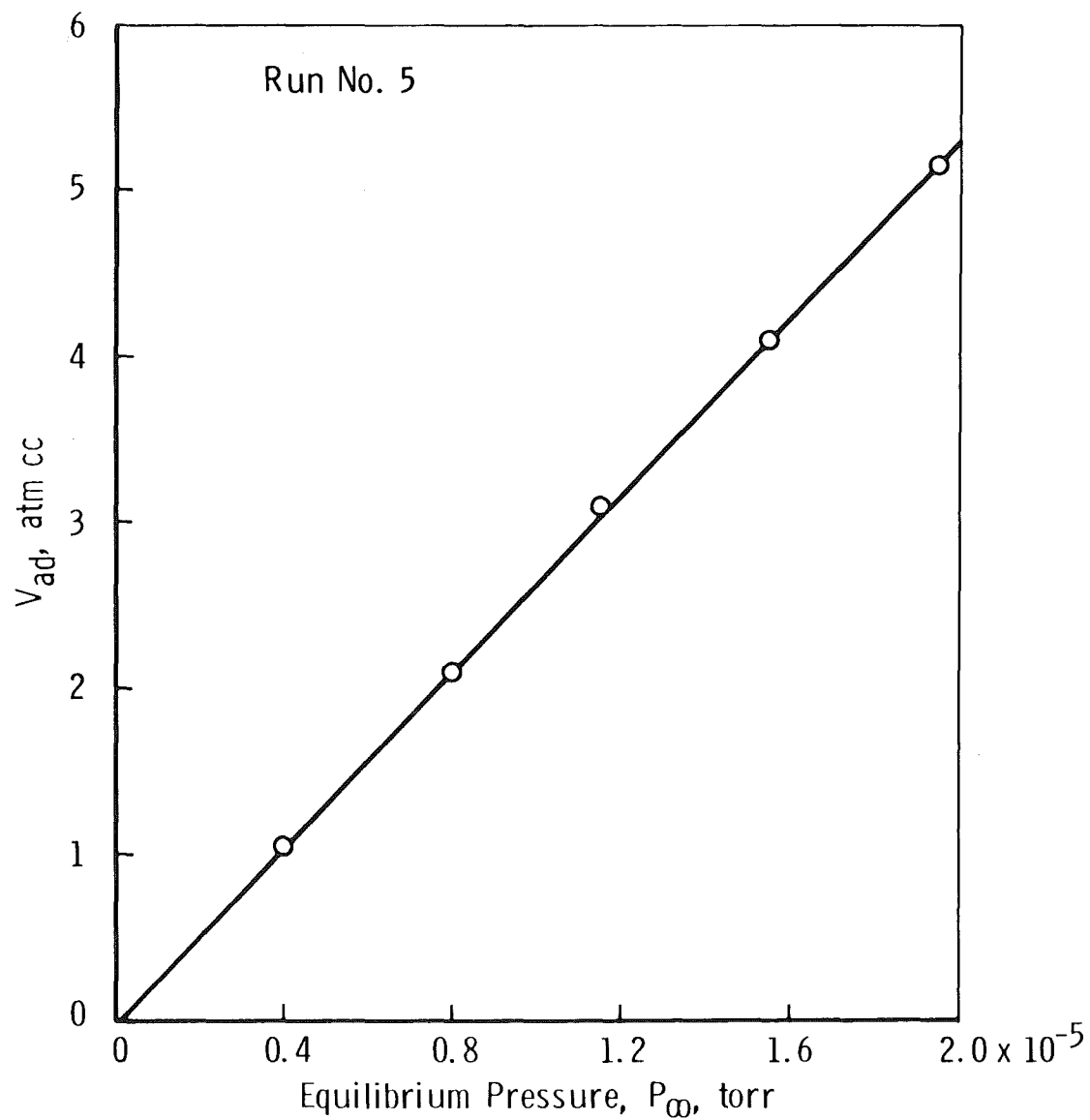


Fig. 7 Adsorption Isotherm Determined for a Discontinuous Run

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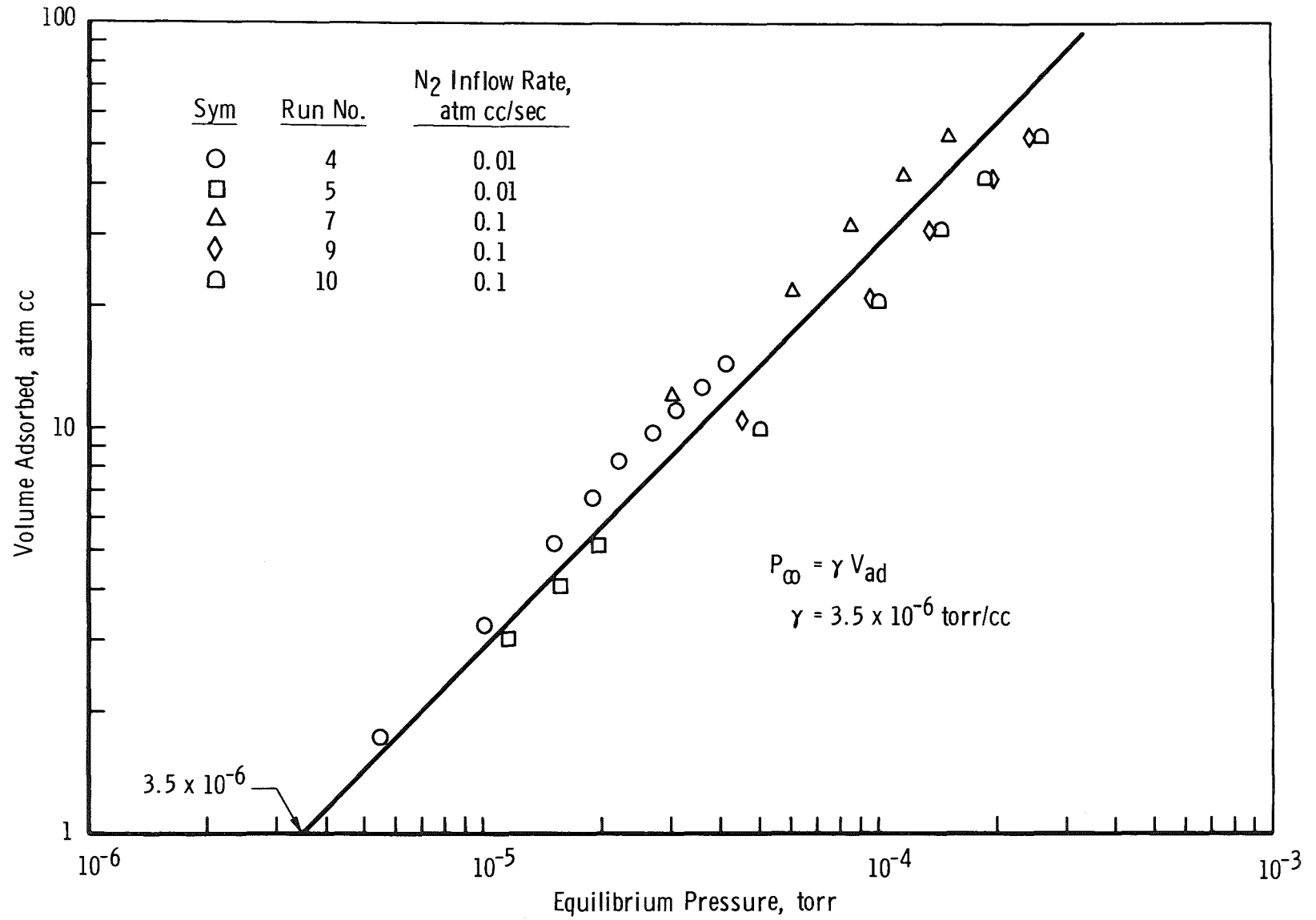
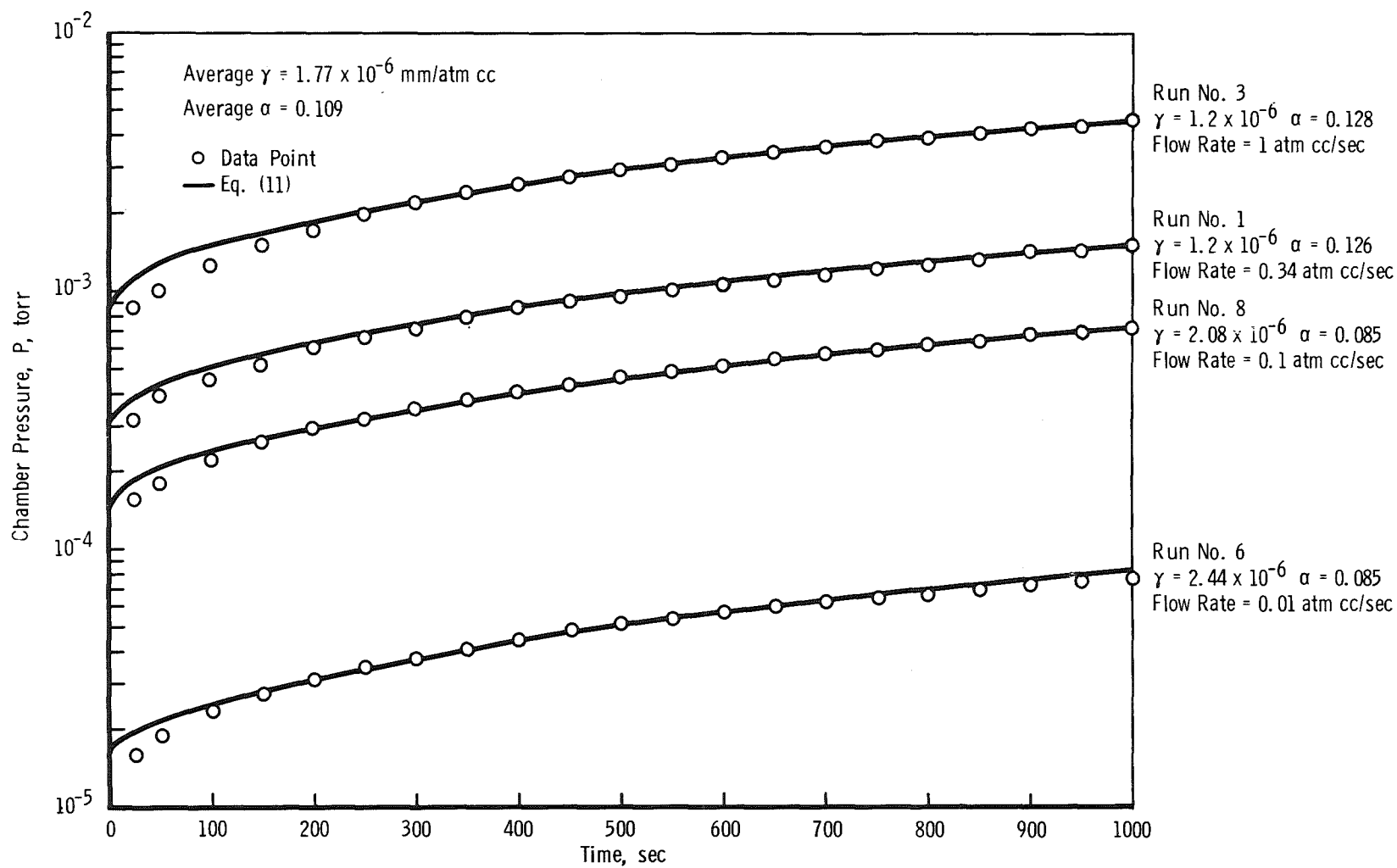
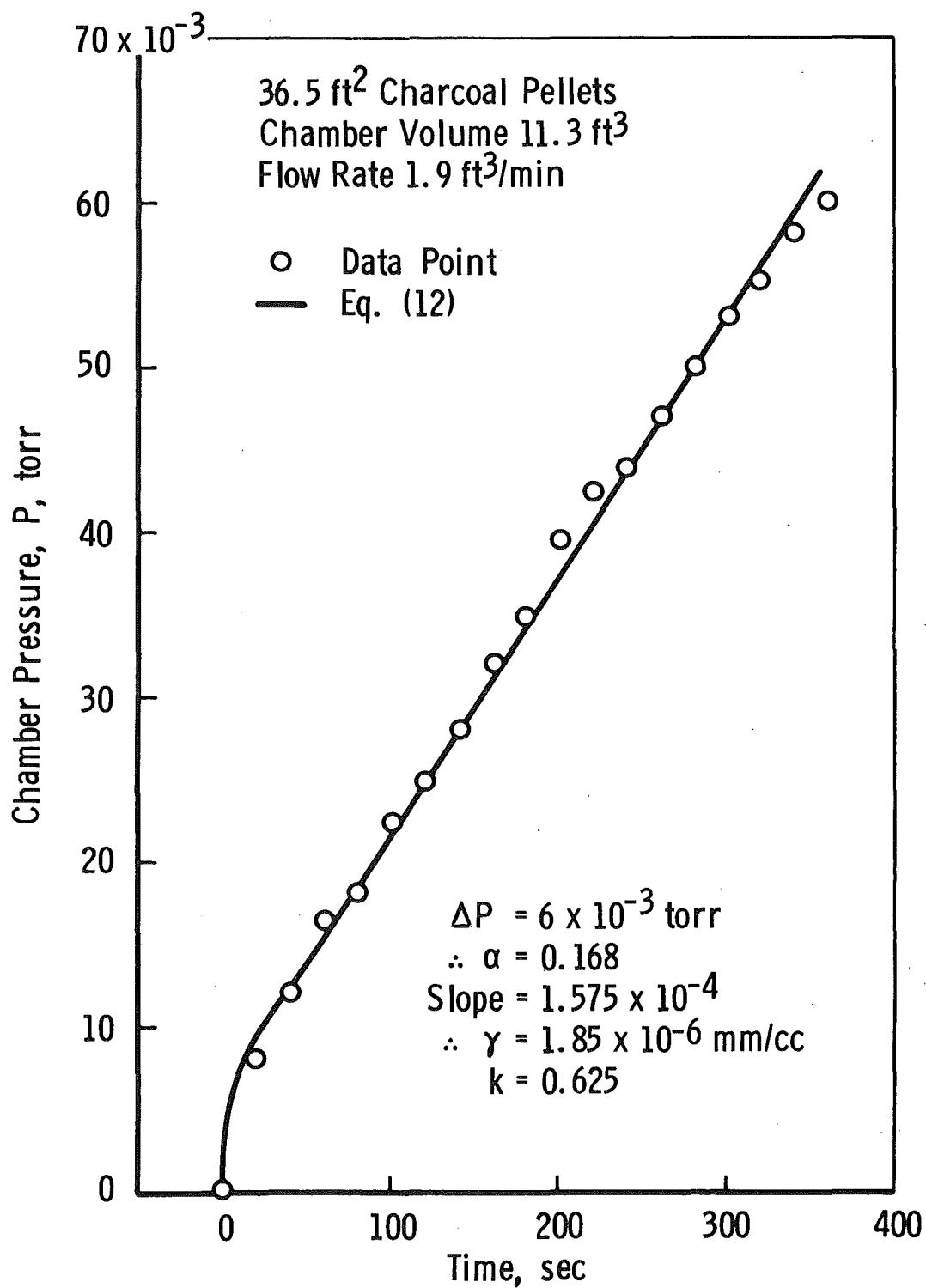


Fig. 8 Adsorption Isotherms for a Collection of Runs

Fig. 9 Determination of γ and α Using Eq. (11)

Fig. 10 Determination of γ and α for a Large Cryosorption Pump, Eq. (12)

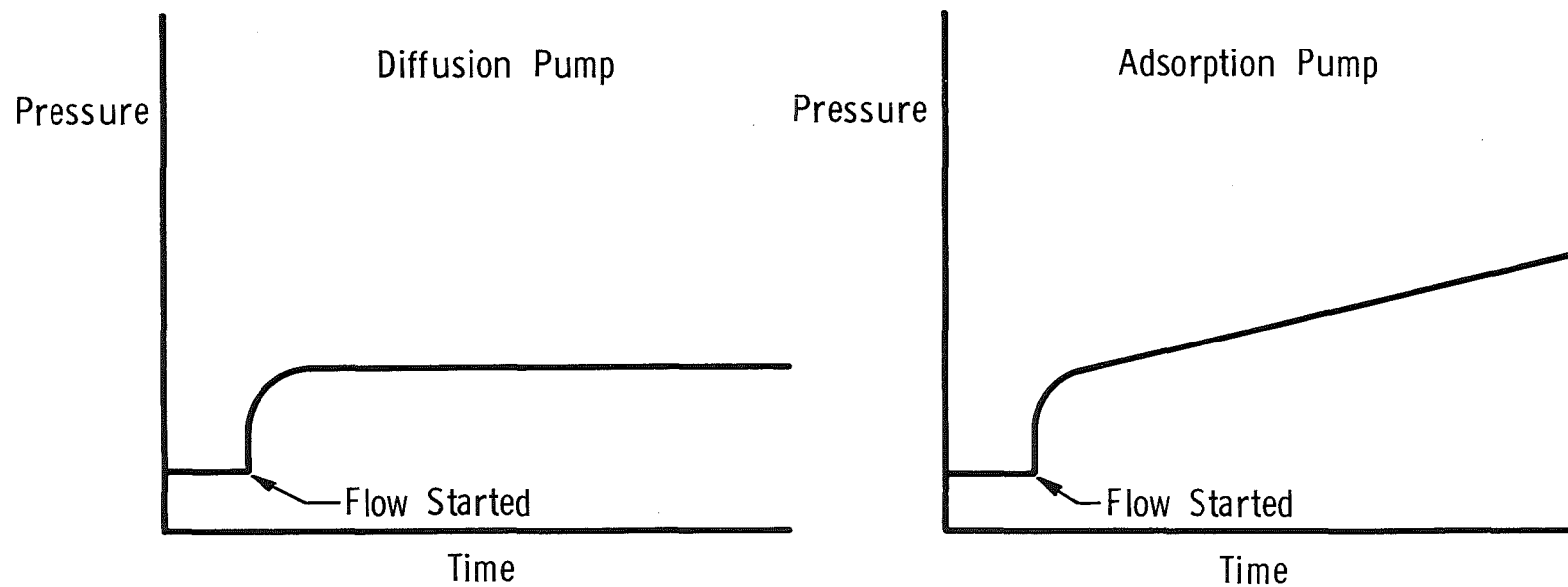


Fig. 11 Comparison between Diffusion Pump and Adsorption Pump for Continuous Inflow